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【Inventor】

【Address】 C/o TOAGOSEI CO., LTD, Nagoya Research
and Development Institute, 1-1, Funamicho, Minato-ku, Nagoya-shi, AICHI,
JAPAN

【Name】 Hiroshi SASAKI
【Inventor】

【Address】 C/o TOAGOSEI CO., LTD, Nagoya Research
and Development Institute, 1-1, Funamicho, Minato-ku, Nagoya-shi, AICHI,
JAPAN

【Name】 Koutarou YONEDA
【Applicant for a Patent】

【Identification Number】 000003034
【Name】 TOAGOSEI CO., LTD
【Representative】 Bunshiro Fukuzawa

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【Document】 Specification 1
【Document】 Abstract 1

Name of Document

Specification

Title of the Invention

CATIONICALLY POLYMERIZABLE LIQUID COMPOSITION

CLAIMS

1. A cationically polymerizable liquid composition comprising:

a cationically polymerizable mixture (A) comprising:

a cyclic ether (A-1) represented by formula (1) below;

a polyfunctional monomer (A-2) having in the molecule at least two cyclic ether groups; and

a latent cationic polymerization initiator (A-3); and

a solid resin (B) that is compatible with the above-mentioned mixture (A) at room temperature and has a softening point of at least 40°C;

the composition having a viscosity at 25°C of 20 Pa sec or below;

and

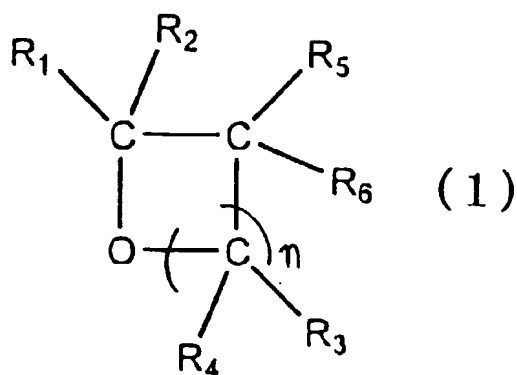
the complex modulus of elasticity (G^*) of the polymer obtained by cationic polymerization satisfies the following relationships at 25°C.

$G^* > 100,000$ (measurement frequency: 0.1 Hz)

$G^* < 4,000,000$ (measurement frequency: 1 Hz)

$G^* > 2,000,000$ (measurement frequency: 100 Hz)

[Chem. 1]

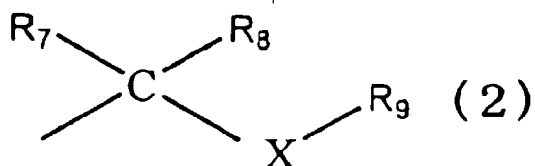


(In formula, n denotes 0, 1, or 2, and R_1 to R_6 independently denote hydrogen

atoms or hydrocarbon groups, which may have a substituent.)

2. The cationically polymerizable liquid composition according to Claim 1 wherein at least one of R_1 to R_6 in formula (1) is a substituent represented by formula (2) below.

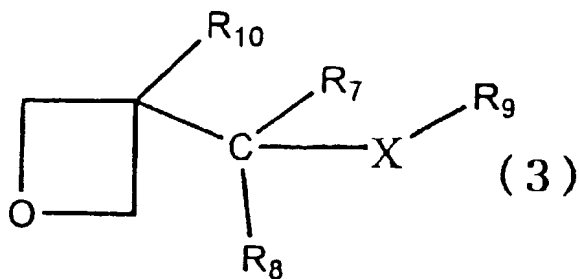
[Chem. 2]



(R_7 and R_8 denote hydrogen atoms or alkyl groups, which may have a substituent, R_9 is a straight- or branched-chain alkyl group that has at least 6 carbon atoms, and X denotes oxygen or $-\text{CH}_2-$.)

3. The cationically polymerizable liquid composition according to Claim 1 or Claim 2 wherein the cyclic ether (A-1) is represented by formula (3) below.

[Chem. 3]



(R_7 , R_8 , R_{10} and X denote the same as in the afore-mentioned formula (2), R_{10} denotes a hydrogen or an alkyl group which may have a substituent.)

4. The cationically polymerizable liquid composition according to any one of Claim 1 to 3 wherein the solid resin (B) is a hydrogenated petroleum resin and/or a hydrogenated rosin derivative.

5. The cationically polymerizable liquid composition according to any one of Claim 1 to 4 wherein the glass transition temperature of the polymer obtained by cationic polymerization is 0°C or below.

6. The cationically polymerizable liquid composition according to any one of Claim 1 to 5 wherein the loss tangent ($\tan \delta$) of the polymer obtained by cationic polymerization is at least 0.8 (measurement frequency: 100 Hz).

DETAILED EXPLANATION OF THE INVENTION

[0001]

Field of the Invention

The present invention relates to a cationically polymerizable liquid composition that, without containing an organic solvent, can be coated easily on a substrate and can be polymerized by light or heat after the coating so that it can be used as a pressure-sensitive adhesive having good tack properties.

[0002]

Description of the Related Art

With regard to conventional pressure-sensitive adhesives, a solvent type in which a rubber or acrylic material is dissolved in an organic solvent, and an emulsion type in which the material is dispersed in water have been used. Currently, solvent type pressure-sensitive adhesives are most widely used, but the release of the organic solvent has become an issue recently.

The emulsion type has the drawbacks of poor water resistance, long drying time, etc. A hot-melt type, which has been proposed as a method for resolving the above-mentioned problems, still has poor coating performance, poor tack properties and, in particular, poor heat resistance.

Recently, a solvent-free liquid curable pressure-sensitive adhesive has been proposed that is formed mainly from a polymerizable monomer, and a large number of proposals have been made regarding a radically photocurable solvent-free liquid composition employing a radically polymerizable acrylate. However, since it is difficult to complete the radical polymerization in air due to the polymerization inhibiting effect of oxygen, the

remaining monomer causes problems such as an unpleasant odor and skin irritation. In order to improve the above-mentioned polymerization, it has been proposed that irradiation with light should be carried out under an atmosphere of nitrogen, but the equipment cost is too high.

A large number of cationically photopolymerizable compositions have been proposed as having good photopolymerization properties in air. For example, JP-A-5-78639 (JP-A denotes Japanese unexamined patent application publication) discloses a pressure-sensitive adhesive comprising a polymer obtained by the copolymerization of acrylic vinyl monomers having a hydroxy group, a bi- or poly-functional epoxy compound, and a cationic polymerization initiator. JP-A-8-60127 discloses a UV curable hot-melt pressure-sensitive adhesive composition comprising a cyclohexene monoepoxide group-containing thermoplastic acrylic polymer, a polyol, and a cationic polymerization photoinitiator. JP-A-11-166168 discloses an acrylic pressure-sensitive adhesive composition comprising an acrylic oligomer obtained by polymerizing specified monomer components, and a cationic photocatalyst. However, since all of these compositions have low polymerizability, a large amount of light is needed when they are cured at room temperature, and the low polymerizability might cause a problem in practice. It is surmised that, since these compositions contain an ester group ascribable to the acrylic group, the presence of the ester group retards the ring-opening polymerization of the cyclic ether, thereby lowering the polymerizability. Furthermore, when the acrylic oligomer has a high molecular weight, the composition becomes highly viscous, thus making it difficult to coat the composition.

[0003]

In order to avoid the retardation in polymerization due to the ester group, a cationically photopolymerizable composition has been disclosed (Eric-Jack Gerard and Jurgen Schneider, Rad. Tech. Europe 97, 175, 1997), the composition employing a material into which an epoxy group had been

incorporated by oxidation of a block polymer having an unsaturated bond in its main chain. JP-A-2000-26830 discloses a UV curable pressure-sensitive adhesive composition formed by mixing a specified epoxy compound, a compound having a functional group that reacts with an epoxy group, a compound having rubber elasticity, and a cationically curing catalyst. However, all of the compositions are very highly viscous; it is proposed in the former that the composition is heated during coating, and in the latter that a solvent is used.

JP-A-11-80681 discloses a foamed pressure-sensitive adhesive tape employing a cationically photoreactive oligomer type pressure-sensitive adhesive composition. Only two types of the composition are disclosed, one of which is the same as that above disclosed by Gerard, et al. and is highly viscous so that it is difficult to coat. The other composition is the same as one disclosed in JP-A-11-166168, and it can be easily expected that its curing speed will be low.

JP-A-11-158437 discloses an adhesion method wherein a pressure-sensitive adhesive material containing a cationically polymerizable compound and a cationic photopolymerization initiator is discharged from a head of an ink-jet printer, coated, and then polymerized by irradiation with light. Although the composition disclosed in the example of the above-mentioned publication has low viscosity, since its polymerizability is low and little polymerization takes place with the level of irradiation described in the publication, it is of no practical utility.

As hereinbefore described, among the solvent-free liquid curable pressure-sensitive adhesives reported so far, there are no reports of a pressure-sensitive adhesive that has ease of coating, can be rapidly polymerized in air and can form a coating of the pressure-sensitive adhesive having good tack properties by irradiation with light.

[0004]

Problems to be Solved by the Invention

It is an object of the present invention to provide a novel cationically polymerizable liquid composition that has ease of coating and high polymerizability in air, and can give a tacky coating having excellent tack properties such as adhesion, holding power, and tack after cationic polymerization.

[0005]

Means to Solve the Problems

As a result of an intensive investigation by the present inventors in order to achieve ease of coating, high polymerizability in air, and good tack properties after polymerization, the present invention has been accomplished by a low viscosity liquid composition comprising a polymerizable mixture comprising a monomer and a latent cationic polymerization initiator, the monomers having as a cationically polymerizable group in the molecule a cyclic ether having ring-opening polymerizability; and a solid resin. The present inventors have found that the viscosity of the liquid composition before polymerization and a specific range of viscoelastic properties of resultant polymers can be adjusted to solve all of the above objects.

In other words, the present invention relates to a cationically polymerizable liquid composition, which is a liquid resin having a viscosity at 25°C of 20 Pa sec or below, comprising a cationically polymerizable mixture (A) comprising a cyclic ether represented by formula (1) below, a polyfunctional monomer (A-2) having in the molecule at least two cyclic ether groups, and a latent cationic polymerization initiator (A-3); and a solid resin (B), and the complex modulus of elasticity (G^*) of the polymer obtained by cationic polymerization satisfies the following relationships at 25°C.

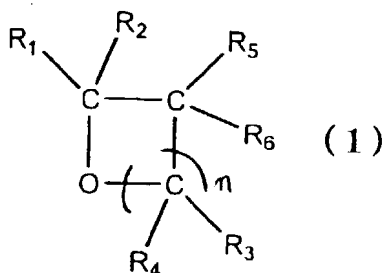
$$G^* > 100,000 \text{ (measurement frequency: 0.1 Hz)}$$

$$G^* < 4,000,000 \text{ (measurement frequency: 1 Hz)}$$

$$G^* > 2,000,000 \text{ (measurement frequency: 100 Hz)}$$

[0006]

[Chem. 4]



[0007]

(In the formula, n denotes 0, 1, or 2, and R₁ to R₆ independently denote hydrogen atoms or hydrocarbon groups, which may have a substituent.)

[0008]

EMBODIMENTS OF THE INVENTION

The present invention is described in detail below.

The glass transition temperature used in the present invention is a value based on the results measured by a DSC measurement method defined by JIS (Japanese Industrial Standards) K 7121. The complex modulus of elasticity is a value based on a measurement obtained by a viscoelasticity measurement method using shear stress.

[0009]

Cationically Polymerizable Mixture (A)

A cationically polymerizable mixture (A) comprises a cyclic ether (A-1) represented by the aforementioned formula (1), a polyfunctional monomer (A-2) having in the molecule at least two cyclic ether groups, and a latent cationic polymerization initiator (A-3).

The above-mentioned components of the cationically polymerizable liquid resin (A) are explained in more detail below.

[0010]

Cyclic Ether (Component A-1)

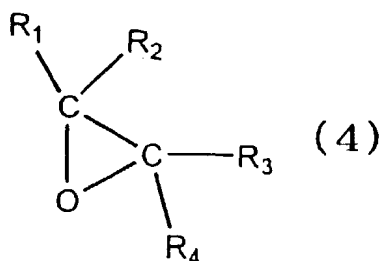
The cyclic ether is used in order to control the viscosity of the composition and the glass transition temperature of a polymer after curing.

The viscosity of the cyclic ether used as the component A-1 is preferably 20 mPa sec or below at 25°C. However, the viscosity of the cyclic ether is not particularly limited as long as the liquid composition finally obtained has a viscosity at 25°C of 20 Pa sec or below.

In detail, compounds having a three-membered epoxy ring, those having a four-membered oxetanyl ring, those having a five-membered tetrahydrofurfuryl ring, etc., represented by formulae (4) to (6) below can be listed.

[0011]

[Chem. 5]

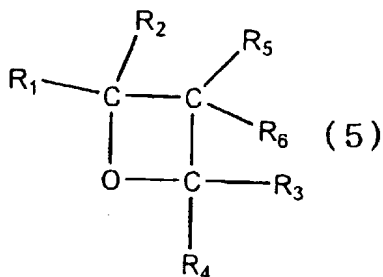


[0012]

(R₁ to R₄ denote hydrogen atoms or hydrocarbon groups, which may have a substituent.)

[0013]

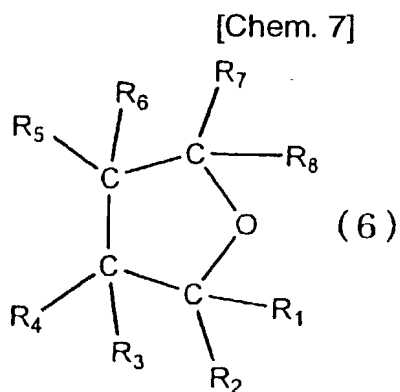
[Chem. 6]



[0014]

(R₁ to R₆ denote hydrogen atoms or hydrocarbon groups, which may have a substituent.)

[0015]



[0016]

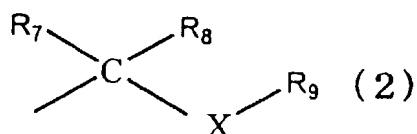
(R₁ to R₈ denote hydrogen atoms or hydrocarbon groups, which may have a substituent.)

[0017]

Among these monomers, it is preferable in the present invention to use a compound in which any one of R₁ to R₆ in the above-mentioned formula (1) is a substituent that is represented by formula (2) below. A cyclic ether represented by formula (3) below is more preferable.

[0018]

[Chem. 8]

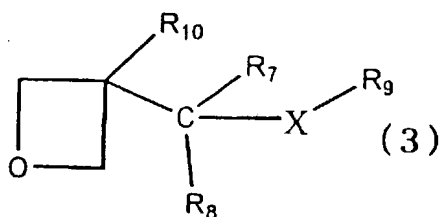


[0019]

(R₇ and R₈ denote hydrogen atoms or alkyl groups, which may have a substituent. R₉ is a straight- or branched-chain alkyl group that has at least 4 carbon atoms, and may have a substituent. X denotes an oxygen atom or -CH₂.)

[0020]

[Chem. 9]



[0021]

(R₇, R₈, R₉ and X are the same as in the aforementioned formula

(2). R₁₀ denotes hydrogen atoms or alkyl groups, which may have a substituent.)

[0022]

Since component A-1 has a comparatively low molecular weight, if there is a large amount of component A-1 remaining in a tacky polymer after polymerization, there is the problem that an unpleasant odor, etc. might occur. Since the use of a monomer having an oxetane ring having high cationic polymerizability can control such a problem to a great extent, it is particularly preferable to use an oxetane compound represented by the above-mentioned formula (3).

[0023]

Polyfunctional Monomer (Component A-2)

Component A-2 is used in order to adjust the viscosity of the composition and the complex modulus of elasticity.

The viscosity of the polyfunctional monomer itself, which is used as component A-2, is not particularly limited as long as the viscosity of the cationically polymerizable liquid composition prepared using the polyfunctional monomer is 20 Pa sec or below.

Specific examples of component A-2 are not particularly limited as long as it is a polyfunctional monomer containing two or more cyclic ether groups in the molecule as represented by the afore-mentioned formula (1), and are exemplified as those generally known as epoxy resins such as bisphenol A epoxy resins, bisphenol F epoxy resins, novolac epoxy resins and alicyclic epoxy

resins, and EKP-207 (trade name; manufactured by Kraton Polymers), which are produced by introducing an epoxy group by oxidizing a block polymer having an unsaturated bond in its main chain, the block polymer being produced commercially by anionic polymerization of an ethylene compound and a diene compound such as butadiene. The examples further include oxetane compounds having at least two four-membered cyclic ether oxetanyl groups in their molecules. However, the present invention is not particularly limited by these examples.

[0024]

Cationic Polymerization Initiator (Component A-3)

The latent cationic polymerization initiator is a compound that can be activated by light or heat to generate an acid component and functions so as to induce the cationic ring-opening polymerization of a group capable of ring-opening polymerization in the composition.

With regard to a cationic polymerization initiator having photolabile properties, any cationic photopolymerization initiator can be used as long as the composition of the present invention can be activated by irradiation with light, thereby inducing the ring opening of a group capable of ring-opening polymerization. Examples of the cationic photopolymerization initiator include onium salts and organometallic complexes.

Examples of the onium salt include diazonium salts, sulfonium salts and iodonium salts. Examples of the organometallic complex include an iron-allene complex, a titanocene complex and an allylsilanol-aluminum complex.

It is also possible to use commercial products such as Optomer SP-150 (trade name; manufactured by Asahi Denka Kogyo K.K.), Optomer SP-170 (trade name; manufactured by Asahi Denka Kogyo K.K.), UVE-1014 (trade name; manufactured by General Electric Company) and CD-1012 (trade name; manufactured by Sartomer Company, Inc.).

[0025]

With regard to the cationic polymerization initiator having thermo-latent properties, any cationic thermopolymerization initiator can be used as long as it can be activated by heating and can induce the ring opening of a group capable of ring-opening polymerization. Examples thereof include various types of onium salt such as quaternary ammonium salts, phosphonium salts and sulfonium salts, and organometallic complexes. As the above-mentioned onium salts, for example, commercial products such as Adeka Opton CP-66 and Adeka Opton CP-77 (both trade names; manufactured by Asahi Denka Kogyo K.K.), San-aid SI-60L, San-aid SI-80L and San-aid SI-100L (all trade names; manufactured by Sanshin Chemical Industry Co., Ltd.) and the CI series (manufactured by Nippon Soda Co., Ltd.) can be used. Examples of the organometallic complexes include alkoxysilane-aluminum complexes.

The mixing ratio of the above-mentioned latent cationic polymerization initiator is preferably in the range of 0.01 to 5 parts by weight relative to 100 parts by weight of the total amount of component A-1 and components A-2. When the mixing ratio of the latent cationic polymerization initiator is less than 0.01 parts by weight, there are cases where the ring-opening reaction of a group capable of ring-opening polymerization cannot be carried out sufficiently even by activation using the action of light or heat, and the tack properties of the polymer so obtained might be inadequate. When the initiator is added at more than 5 parts by weight, the effect of promoting the polymerization cannot be further enhanced, and the initial tack strength might even be degraded.

[0026]

Solid Resin (B)

The solid resin (B) has a softening point of at least 40°C, is compatible with the above-mentioned cationically polymerizable liquid resin (A) at room temperature, and is a component that adjusts the viscoelastic characteristics of the polymer. Adding the solid resin (B) to the cationically

polymerizable liquid resin (A) can reduce the complex modulus of elasticity at low frequency (e.g., ca. 1 Hz) and can increase the complex modulus of elasticity at high frequency (e.g., ca. 100 Hz). A compound that is generally known as a tackifier can be used.

With regard to the solid resin (B), a solid resin that is generally known as a tackifier and has a comparatively low molecular weight and a high softening point can be used. For example, a tackifier such as a rosin resin, a modified rosin resin, a hydrogenated rosin resin, a terpene resin, a terpene phenol resin, an aromatic modified terpene resin, a C₅ or C₉ petroleum resin and a hydrogenated derivative thereof, or a chroman resin can be used. However, the solid resin (B) is not particularly limited by the above-mentioned resins as long as it is compatible with the aforementioned cationically polymerizable mixture (A) at room temperature and has a softening point of at least 40°C.

Among the above-mentioned resins, a hydrogenated rosin resin and a hydrogenated petroleum resin are preferable in terms of their excellent compatibility with the cationically polymerizable mixture (A), improved transparency of the pressure-sensitive adhesive after curing, and their ability to exhibit a strong adhesive power.

[0027]

Viscosity

The viscosity of the cationically polymerizable liquid composition is 20 Pa sec or below at 25°C. When the composition has a higher viscosity than the above-mentioned range, it becomes difficult to coat at room temperature and heating is required in some cases. Since heating a latent cationically polymerizable composition generally degrades its stability and increases the viscosity, heating is not desirable. In order to obtain good coating performance, the viscosity at 25°C is preferably 10 Pa sec or below.

[0028]

Viscoelastic characteristics

The complex modulus of elasticity (G^*) of the cationic polymer obtained by cationic polymerization of the above-mentioned composition preferably has viscoelastic characteristics at 25°C that satisfy the following conditions at each frequency.

$G^* > 100,000$ (measurement frequency: 0.1 Hz)

$G^* < 4,000,000$ (measurement frequency: 1 Hz)

$G^* > 2,000,000$ (measurement frequency: 100 Hz)

When the complex modulus of elasticity at 0.1 Hz is less than 100,000, the cohesive strength of the polymer becomes undesirably low. When the polymer is peeled off from an adherend, cohesive failure takes place, thereby causing a so-called 'glue residue'. An undesirable reduction in holding power might also occur in some cases. The complex modulus of elasticity at 0.1 Hz is more preferably 200,000 or above.

When the complex modulus of elasticity at 1 Hz is more than 4,000,000, the polymer becomes hard and it undesirably shows no initial adhesion. It is more preferable for the complex modulus of elasticity at 1 Hz to be 3,000,000 or below.

When the complex modulus of elasticity at 100 Hz is less than 2,000,000, the tack value, which is essential for a pressure-sensitive adhesive, decreases. It is more preferable for the complex modulus of elasticity at 100 Hz to be 3,000,000 or above.

In order to obtain a high tack value it is preferable for the loss tangent ($\tan \delta$) at 25°C to be at least 0.8 (measurement frequency: 100 Hz), and more preferably at least 1.0.

[0029]

Glass transition temperature

When the glass transition temperature of a polymer obtained by polymerizing cationically the composition of the present invention is equal to 0°C or above, it becomes difficult to maintain the above-mentioned viscoelastic

characteristics, and it is therefore preferable for the glass transition temperature to be equal to 0°C or below, and more preferably -20°C or below.

[0030]

Other additives

The composition of the present invention can contain, in addition to the above-mentioned cationically polymerizable mixture (A) and solid resin (B), a known plasticizer, anti-aging agent, filler, etc. as appropriate in amounts that do not interfere with the objects of the present invention. In order to enhance the coating performance, a viscosity increasing agent such as an acrylic rubber, an epichlorohydrin rubber, an isoprene rubber or a butyl rubber, a thixotropic agent such as colloidal silica or polyvinylpyrrolidone, a filler such as calcium carbonate, titanium oxide or clay, etc. can be added.

With the aim of imparting high adhesive shear strength, it is possible to add hollow inorganic materials such as glass balloons, alumina balloons or ceramic balloons; organic spheres such as nylon beads, acrylic beads or silicone beads; hollow organic materials such as vinylidene chloride balloons or acrylic balloons; and filaments such as glass, polyester, rayon, nylon or cellulose. When adding the above-mentioned glass filaments, although it is possible to add fibrous chips to the composition, carrying out the polymerization by impregnating a woven glass with the above-mentioned photopolymerizable composition, etc. can achieve very high adhesive shear strength.

[0031]

When using the tackifying liquid composition of the present invention, for example, paper, plastic laminated paper, cloth, plastic laminated cloth, plastic film, metal foil, a foamed material, etc. is used as a support, the pre-polymerization tackifying composition is coated on one side or both sides of the support by an appropriate coating means such as a comma roll, a gravure coater, a roll coater, a kiss coater, a slot die coater, or a squeeze coater, the polymerization is effected by the application of heat or light, and a pressure-

sensitive adhesive layer is formed so as to have a thickness of usually 10 to 500 μm per side to give a pressure-sensitive adhesive sheet in tape form, sheet form, etc.

[0032]

There is no particular limitation on the light source that can be used for carrying out polymerization by irradiation with light. Light sources having an emission distribution that extends to a wavelength of 400 nm or below can be used. Examples thereof include a low-pressure mercury lamp, a medium-pressure mercury lamp, a high-pressure mercury lamp, a superhigh-pressure mercury lamp, a fluorescent lamp, a black light lamp, a microwave-excited mercury lamp and a metal halide lamp. The intensity of the light that irradiates the tacky polymer is controlled according to the target product and is not particularly limited, but it is preferable for the light intensity in the light wavelength region that is effective in activating the photo-latent initiator (depending on the photopolymerization initiator, but usually light at 300 to 420 nm) to be 0.1 to 100 mW/cm^2 . When the intensity of light that irradiates the tacky composition is less than 0.1 mW/cm^2 , the reaction time becomes too long. When it exceeds 100 mW/cm^2 , there is a possibility that the heat radiated from the lamp and the heat generated during polymerization of the composition might reduce the cohesive strength of the pressure-sensitive adhesive layer so obtained, yellow the layer, and degrade the support.

The duration for which the light irradiates the tackifying composition is controlled according to the target product and is not particularly limited, but it is preferable to set the duration so that the accumulated amount of light represented by the product of the intensity and the duration of the irradiation with light in the above-mentioned light wavelength region is 10 to 5,000 mJ/cm^2 . When the accumulated amount of light that irradiates the above-mentioned tackifying composition is less than 10 mJ/cm^2 , active species cannot be generated sufficiently from the photo-latent initiator, thereby raising the possibility

that the tack properties of the pressure-sensitive adhesive layer so obtained might be degraded. When it exceeds 5,000 mJ/cm², the irradiation time becomes very long and it is disadvantageous in terms of productivity.

When polymerization is carried out using heat, the heat can be applied by a standard method and the conditions therefor are not particularly limited.

[0033]

Examples

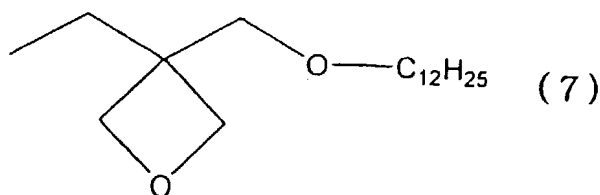
The present invention is explained in more detail below by reference to examples, but the present invention is in no way limited thereby.

Example 1

Oxetane monomer OXR-12 (manufactured by Toagosei Co., Ltd.) represented by the aforementioned formula (7) and having an alkyl group of 12 carbons in a side chain, polyfunctional monomer EKP-207 (trade name; manufactured by Kraton Polymers;), iodonium salt photo-latent cationic initiator 2074 (trade name; manufactured by Rhodia Inc.), and hydrogenated petroleum resin Regalite 1090 (trade name; manufactured by Hercules, Inc.) having a softening point of about 90°C were uniformly mixed at 40°C in the composition ratio shown in Table 1 below to give a cationically polymerizable liquid composition.

[0034]

[Chem. 10]



[0035]

The composition so obtained was coated on a 50 μm thick polyethylene terephthalate film (PET film) using a doctor blade so as to give a

coating thickness of about 25 μm , and then irradiated with ultraviolet rays (135 mJ/cm^2) by feeding it once at a conveyor speed of 10 m/min under a 120 W/cm condenser type high-pressure mercury lamp (lamp height: 10 cm) thereby effecting cationic polymerization to form a pressure-sensitive adhesive layer and give a pressure-sensitive adhesive sheet.

In order to measure the viscoelastic properties, the composition was also poured on a sheet of Teflon so as to give a thickness of 1 mm, polymerized under the same irradiation conditions as for preparation of the pressure-sensitive adhesive sheet, and then released from the Teflon sheet to give a polymer for evaluation.

[0036]

Examples 2 to 6 and Comparative Examples 1 to 3

The compositions of Examples 2 to 6 and Comparative Examples 1 to 3 were obtained in the same manner as in Example 1 except that the compositional ratios were changed as shown in Table 1. L-1203 (manufactured by Kraton Polymer) is a fully saturated monool having a molecular weight of 3,600 that is produced by hydrogenating a straight-chain poly(ethylene/butylene) having one terminal hydroxy group and does not correspond to component A-2 of the present invention. Regalite 1125 (manufactured by Hercules, Inc.) is a hydrogenated petroleum resin having a softening point of about 125°C .

Each of these compositions was used in the same manner as in Example 1 to give polymers for the measurement of viscoelasticity and pressure-sensitive adhesive sheets on PET film. In Comparative Example 3, since each component of the composition is highly viscous, the components other than the photo-latent initiator were dissolved at 100°C , and the photo-latent initiator was then dissolved at 80°C . When preparing a polymer for the measurement of viscoelasticity and a pressure-sensitive adhesive sheet on a PET film using the above-mentioned composition, the composition continued being heated at 80°C so as to reduce the viscosity, and an obvious increase in viscosity was observed.

Therefore, immediately after dissolving the initiator only the viscosity was measured, and the other evaluations were suspended.

[0037]

[Table 1]

	Example						Comparative		
	1	2	3	4	5	6	1	2	3
Oxetane OXR-12	80	80	80	80	70	70	80	85	
EKP-207	20	20	20	20	30	30	20	15	60
2074 (Rhodia)	1	1	1	1	1	1	1	1	1
Regalite 1090	120	140			100	120		130	100
Regalite 1125			60	67.5					
L-1203									40

[0038]

The viscosity of the compositions prepared in the above-mentioned examples 1 to 6 and comparative examples 1 and 3, the glass transition temperature and the viscoelastic characteristics of the polymers, and the tack properties (tack strength, holding power, probe tack) of the pressure-sensitive adhesive sheets were measured by the methods below. The results from measurement of the viscosity and the viscoelasticity are given in Table 2, and the results from measurement of the tack properties are given in Table 3. In comparative example 3, since the viscosity increase occurred as described above, only the result from measurement of the viscosity is given.

Viscosity measurement: the viscosity of a composition after mixing was measured at 25°C using an E type viscometer.

Viscoelasticity measurement: the complex modulus of elasticity in terms of sheer stress of the cationic polymer obtained from a composition was

measured on a 1 mm thick polymer in an RDSII type viscoelastometer manufactured by Rheometrics, Inc.

Glass transition temperature: the above-mentioned polymers were subjected to a DSC method in accordance with JIS K 7121.

Tack strength: measured by a method in accordance with JIS Z 0237. A pressure-sensitive adhesive sheet was cut to a width of 25 mm, then bonded to an adherend (SUS sheet or polyethylene (PE) sheet) through an adhesion area of 25 mm x 100 mm, and compression bonded by a double pass of a 2 kg roll. The peel strength at 180° was measured at 23°C and 65% RH. The state of the pressure-sensitive adhesive remaining on the adherend after the peel strength measurement was examined; when the peel state was of the interfacial peel type, it was denoted by A, and when the pressure-sensitive adhesive remained on the adherend, it was determined that cohesive failure had taken place, and it was denoted by C.

Holding power: a sample (25 mm width) cut out from the pressure-sensitive adhesive sheet was affixed to an SUS sheet through an adhesion area of 25 mm x 25 mm and compression bonded by a double pass of a 2 kg roll. A 1 kg load was applied at 40°C and 100°C and the time taken for the sheet to peel off was measured as the holding time, which represented the holding power. When the sheet was held after 24 hours, the holding time was denoted by 'at least 24 hours', and the creep from the initial attachment position was also measured and the value recorded. With regard to the samples that had peeled off within 24 hours, the state of the pressure-sensitive adhesive remaining on the adherend after the measurement was examined; when the peel state was of the interfacial peel type, it was denoted by A, and when the pressure-sensitive adhesive remained on the adherend, it was determined that cohesive failure had taken place, and it was denoted by C.

Probe tack: the probe tack was measured in accordance with ASTM D 2979 under the following conditions.

Probe: 5 mm diameter SUS #400 polished surface

Load: 100 g/cm²

Contact time: 1 sec

Probe speed: 1 cm/sec

Measurement was carried out five times per sample, and the average value is given.

[0039]

[Table 2]

Table 2: The viscosity, the glass transition temperature and the viscoelastic characteristics of the polymers.

	Example					
	1	2	3	4	5	6
Viscosity (mPa s)	3900	6500	1000	1500	4400	7300
Tg (°C)	-29.9	-26.3	-42.1	-39.8	-37.0	-31.2
G* (0.1 Hz)	2.4E+05	2.0E+05	4.5E+05	4.3E+05	2.9E+05	3.8E+05
G* (1 Hz)	5.2E+05	7.1E+05	6.0E+05	6.4E+05	3.8E+05	5.6E+05
G* (100 Hz)	6.2E+06	7.3E+06	2.1E+06	2.2E+06	2.1E+06	3.2E+06
Tan δ (100 Hz)	2.6	3.2	1.2	1.4	1.6	2.2

[Table 2] (Continued)

	Comparative		
	1	2	3
Viscosity (mPa s)	370	4200	327000
T _g (°C)	-47.5	-29.7	-
G* (0.1 Hz)	3.0E+05	9.0E+04	-
G* (1 Hz)	3.5E+05	2.8E+05	-
G* (100 Hz)	6.8E+05	3.8E+06	-
Tan δ (100 Hz)	0.6	3.1	-

[0040]

[Table 3]

Table 3: The tack properties

	Example					
	1	2	3	4	5	6
Adhesion (g/inch)						
SUS	1220, A	1460, A	550, A	620, A	520, A	1000, A
PE	550, A	640, A	143, A	170, A	220, A	375, A
Holding power						
(holding time,	>24 hr	>24 hr	>24 hr	>24 hr	>24 hr	>24 hr
creep)	0 mm	0 mm	0 mm	0 mm	0 mm	0 mm
Probe tack (gf)	755	503	621	513	557	532

[Table 3] (Continued)

	Comparative		
	1	2	3
Adhesion (g/inch)			
SUS	20, A	1850, C	-
PE	11, A	950, A	-
Holding power			
(holding time,	>24 hr	>24 hr	-
creep)	0 mm	4.2 mm	-
Probe tack (gf)	53	1170	-

[0041]

As shown in Table 2, the compositions of Examples 1 to 6 and Comparative Example 1 to 2 had low viscosities, and they could easily be coated when preparing the pressure-sensitive adhesive sheets, whereas the composition of Comparative Example 3 had a high viscosity and it was difficult to coat at room temperature. When it was heated so as to reduce the viscosity, there was an obvious increase in viscosity, probably as a result of polymerization due to insufficient thermal stability.

As shown in Table 2, in the case of the composition of Comparative Example 1, which gave a polymer whose complex modulus of elasticity at 100 Hz was outside the range of viscoelasticity defined in the present invention, the tack value greatly decreased, and as a result the tack strength was poor.

As shown in Comparative Example 2, when the composition gave rise to a polymer deviated from the range determined by the present invention in the viscoelastic properties of the polymer, particularly in the complex

modulus of elasticity at 0.1 Hz , the cohesive force of the polymer was lowered and a lowered holding power and cohesion failure in separation were resulted.

As is clear from the above-mentioned table 3, the pressure-sensitive adhesive compositions of Examples 1 to 6 all showed excellent tack properties and, in particular, good holding power. The peel state was of the interfacial peel type in all the examples, and there was no pressure-sensitive adhesive remaining on the adherends.

It has been found from the above-mentioned results that the compositions that satisfy the viscosity and viscoelastic characteristics defined as being preferable in the present invention can be easily coated on a substrate at room temperature and the polymers obtained by cationic polymerization have good tack properties.

[0042]

Advantageous effect of the Invention

The cationically polymerizable liquid composition of the present invention can, without containing a solvent, be coated easily on a substrate and can be used as a pressure-sensitive adhesive having good tack properties by the application of light or heat after coating. There is a high expectation that these novel pressure-sensitive adhesives that do not require an organic solvent to be removed will replace existing solvent type pressure-sensitive adhesives.

Abstract

Problems

It is an object of the present invention to provide a novel cationically polymerizable liquid composition that, without containing an organic solvent, can be coated easily on a substrate and so that it can be used as a pressure-sensitive adhesive having good tack properties.

Means to Solve the Problems

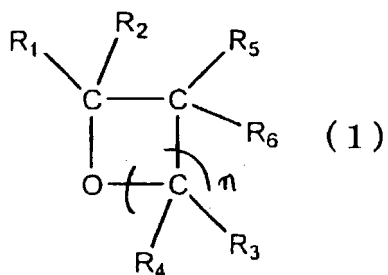
A cationically polymerizable liquid composition comprising:
a cationically polymerizable mixture (A) comprising:
 a cyclic ether (A-1) represented by formula (1) below;
 a polyfunctional monomer (A-2) having in the molecule at least two cyclic ether groups; and
 a latent cationic polymerization initiator (A-3); and
a solid resin (B) that is compatible with the above-mentioned mixture (A) at room temperature and has a softening point of at least 40°C;
 the composition having a viscosity at 25°C of 20 Pa sec or below;
and
 the complex modulus of elasticity (G^*) of the polymer obtained by cationic polymerization satisfies the following relationships at 25°C.

$$G^* > 100,000 \text{ (measurement frequency: 0.1 Hz)}$$

$$G^* < 4,000,000 \text{ (measurement frequency: 1 Hz)}$$

$$G^* > 2,000,000 \text{ (measurement frequency: 100 Hz)}$$

[Chem. 1]



(In formula, n denotes 0, 1, or 2, and R_1 to R_6 independently denote hydrogen atoms or hydrocarbon groups, which may have a substituent.)

Representative drawing

None.